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SOLUBILITY OF NYLON IN
METHANOL-WATER SOLUTIONS

RAYMOND S. TUSZNSKI

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SOLUBILITY OF NYLON IN
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Raymond S. Tuszynski

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METHANOL-WATER SOLUTIONS

by

Raymond S. Tuszynski
Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN

CHEMISTRY

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ABSTRACT

The solubility of nylon in a vehicle such as methanol and water, is a factor that must often be considered when nylon is to be employed as a binder to improve certain properties of the end products of processing or manufacturing.

Solubility curves for 'LYTEL' 63, a type of nylon, in methanol-water solutions were determined at a temperature of 25 °C. One curve shows the solubility range for nylon solutions prepared at a temperature of 25 °C while the other is a representative curve showing the range for solutions prepared by cooling nearly critical solutions to 25 °C. The data for the latter curve in the 60-100% range were not reproducible and appear to depend upon variables involved in the preparation of the systems.

The curves coincide in the lower solubility range but diverge in the higher range. Each of the curves shows that the solubility of 'ZYTEL' 63 increases with the addition of water to methanol, reaches a maximum when the concentration of methanol is about 82% and then decreases.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor Melvin F. Reynolds of the U. S. Naval Postgraduate School.

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1. Introduction

A binder confers desirable properties, such as plasticity, on certain materials. It is frequently added to those materials by the technique of precipitation.

Initially, a lacquer is prepared by dissolving the binder in an organic solvent, such as methanol. The addition of water to the lacquer causes the precipitation of the binder and the precipitated particles are attracted to and deposit on the particles of the unplasticized material. The final plasticized material can then be pressed to any desired shape or form.

In the process described above the nylon can function as the binder. From a processing standpoint the solubility curve for nylon in methanol-water solutions would be desirable. Consequently, investigative work was carried out to determine such a curve at 25 °C.

Two methods were employed to secure the necessary data for the curves. In one method equilibrium at 25 °C was approached from the unsaturated side while in the second method equilibrium was approached by cooling nearly critical solutions from elevated temperatures to 25 °C.

'ZYTEL' 63, manufactured by DUPONT Co., was the type of nylon used while methanol was selected because it is characteristic of the organic solvents that are used for dissolving nylon.

2. Description of Apparatus

The apparatus that provided for continuous agitation of the systems at a constant temperature is shown on page 3. Essentially, it consisted of two plastic 18 inch wheels submerged in a thermostat controlled water bath. Driving power was provided by a DC variable speed motor via a pulley and belt arrangement. Metal bearing surfaces being wholly submerged in water presented a corrosive and shaft binding problem. This difficulty was overcome by the use of plastic bearing surfaces which proved to be most satisfactory in view of the fact that the apparatus ran continuously for four months without maintenance. Glass stoppered flasks and test tubes, containing the nylon systems, were attached to the submerged wheels. Thus, the systems were continually agitated at constant temperature.

Filtering of samples for analysis was initially accomplished using the conventional vacuum filtering technique. This introduced some small error due to the fact that some of the solvent was evaporated during filtering. Methanol was subjected to the same filtering conditions that were used for the samples and the resulting loss was determined. This loss in weight due to evaporation showed that the results obtained could be in error to the extent of 2-3% for the more viscous solutions that required considerable time for filtering.

To eliminate this source of error filtering was accomplished by a simple pressure filtering device as shown on page 4. This latter technique proved successful because it reduced solvent loss to a negligible amount and also made it possible to filter the more viscous solutions which could not be filtered by the former technique.

Other equipment employed was of the conventional type.

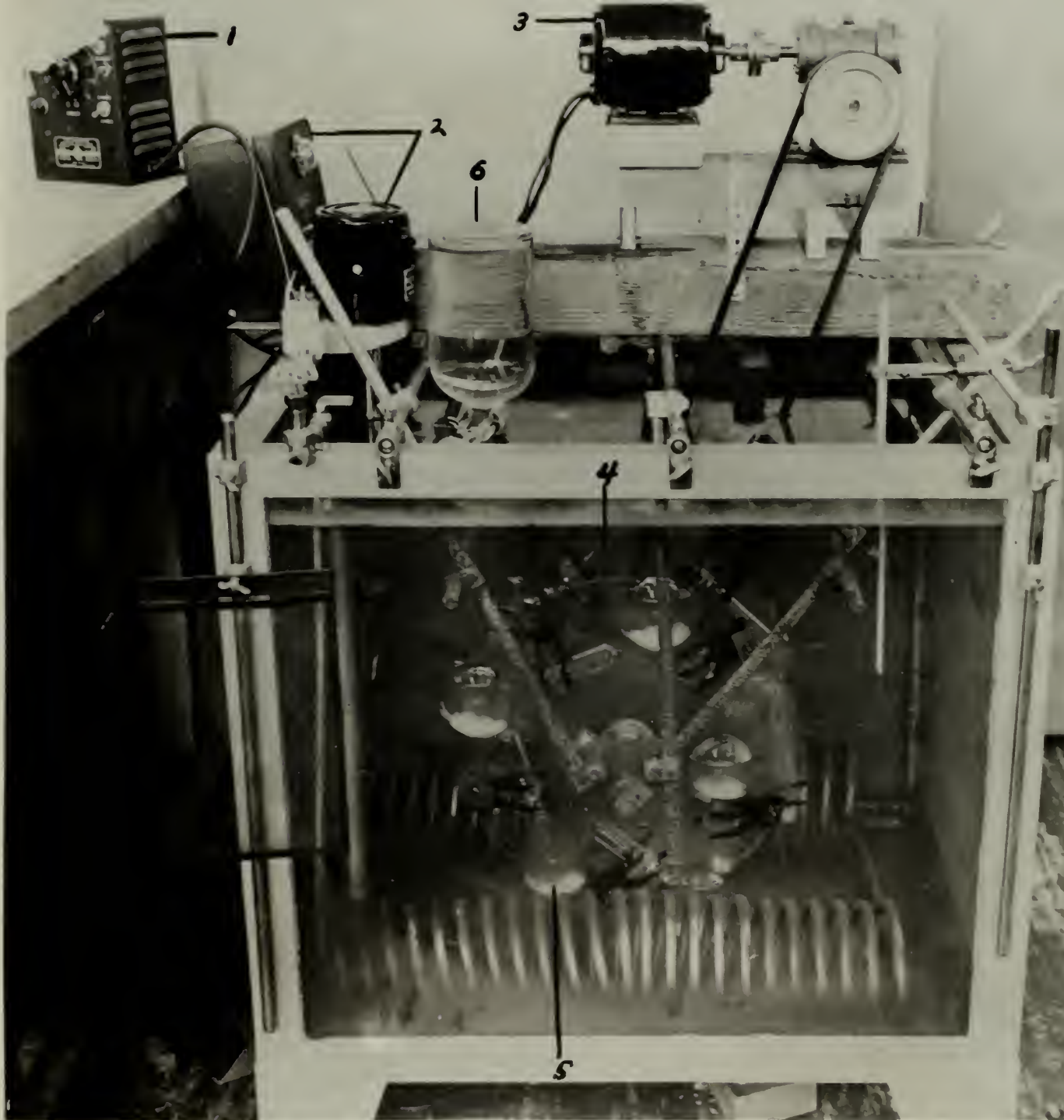


FIGURE 1

- 1 - VARIAC CONTROL
- 2 - THERMOSTAT CONTROL and AGITATOR
- 3 - D.C. VARIABLE SPEED MOTOR and GEAR REDUCTION UNIT
- 4 - PLASTIC SUBMERGED WHEELS
- 5 - NYLON SOLUTIONS
- 6 - UNIT for CONTROLLING WATER LEVEL in BATH

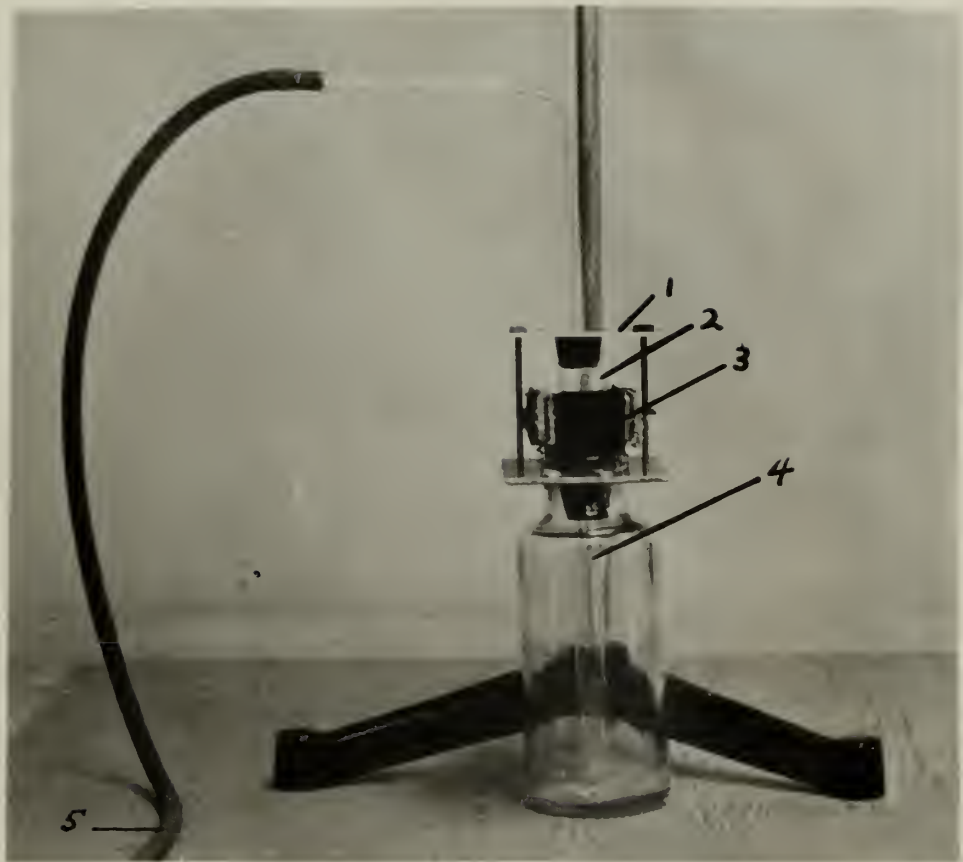


FIGURE 2

- 1 - YOKE ASSEMBLY
- 2 - SINTERED GLASS CRUCIBLE
- 3 - FILTERING FUNNEL
- 4 - TEST TUBE
- 5 - CONNECTION TO PRESSURE SOURCE

3. General Laboratory Procedure

As previously mentioned in the Introduction two methods were employed in order to secure the necessary data.

In one method 200 cc methanol-water solutions of varying concentrations were prepared. The component amounts were measured by calibrated pipettes. Ten to fifteen grams of 'ZYTEL' 63 resin* were added to the different methanol-water solutions at room temperature. The resulting systems in glass stoppered flasks were then placed on the submerged wheels of the 'Water Wheel' Apparatus¹ and continually agitated at 25 °C. Some of the solutions remained in the 'Water Wheel' Apparatus for four months and others for lesser periods. Samples were taken periodically and filtered through a size M sintered glass crucible. The filtrate was weighed, and the methanol and water evaporated in an oven at 65 °C. The residue was then dried in the oven at 65 °C to a constant weight.

In the other method 200 cc methanol-water solutions of varying concentrations were prepared in the same manner as in the first method. Ten to fifteen grams of 'ZYTEL' 63 resin* were added to each of the methanol-water solutions at room temperature. The resulting systems in glass stoppered flasks were heated in a water bath at a temperature of 65 °C for 60 minutes. They were placed on the submerged wheels of the 'Water Wheel' Apparatus which operated under the same conditions as described for the first method. Subsequent procedure was identical to that used in the first method.

* The 'Zytel' 63 resin used was not oven dried. When oven dried at a temperature of 65 °C a 2.7% loss in weight was observed.

¹The apparatus as shown on page 3.

4. Results

The solubility data at 25 °C for nylon ('ZYTEL' 63) in methanol-water solutions are summarized in Tables 1 and 2.

Both sets of data are illustrated graphically in Figure 4.



Solubility of Nylon ('ZYTEL' 63) in Methanol-Water Solutions at 25 °C

Obtained by Approaching Equilibrium from Unsaturated Side.

<u>Methanol in Methanol-Water</u> <u>Solvent, % by Weight</u>	<u>Nylon - Parts by Weight per</u> <u>100 Parts by Weight of Meth-</u> <u>anol-Water Solvent</u>
100.0	0.803
93.9	0.965
86.6	0.988
82.1	1.105
76.5	0.647
74.0	0.475
61.9	0.135
50.4	0.107
39.4	0.076
28.9	0.053

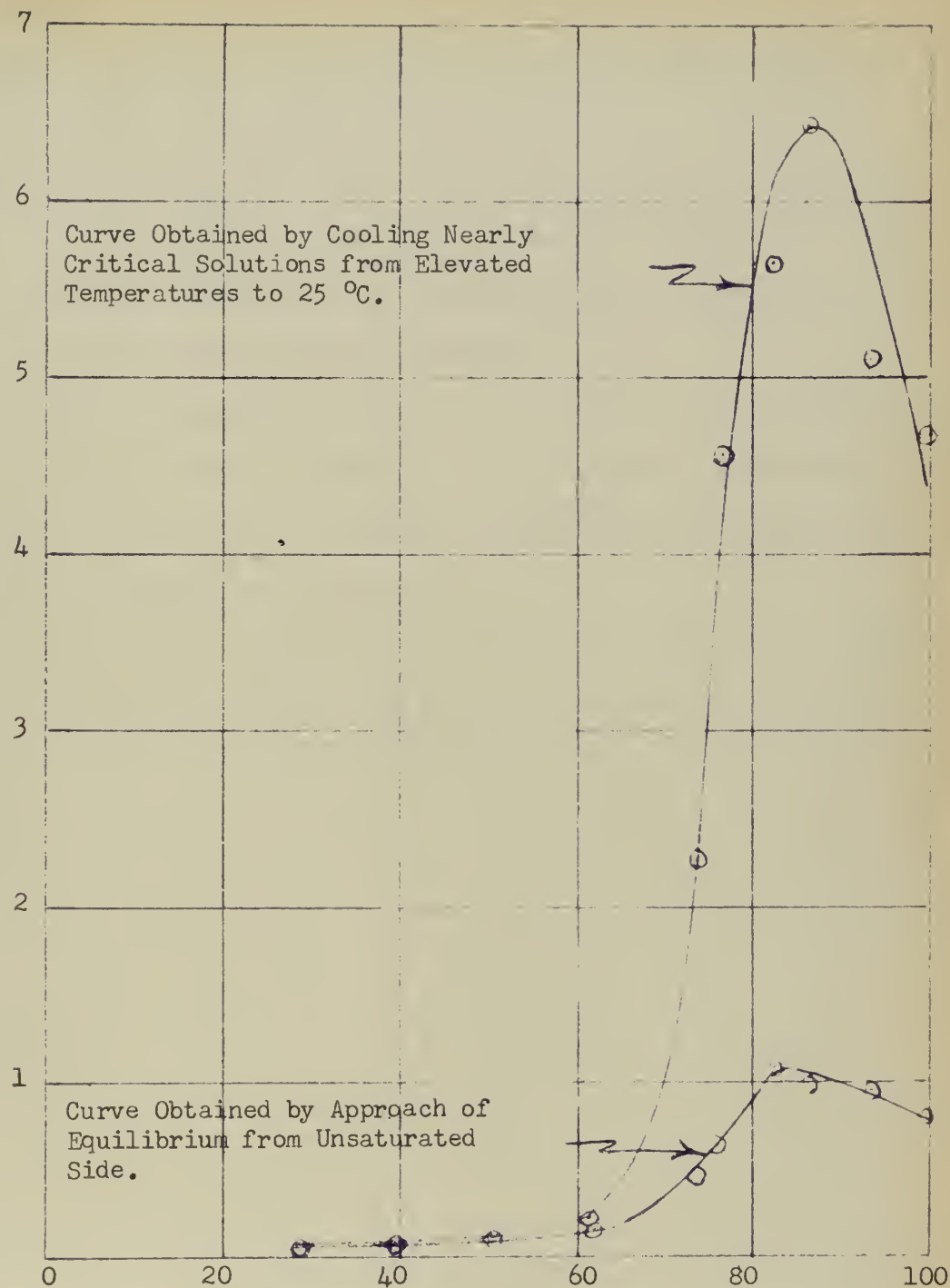
Table 1

Solubility of Nylon ('ZYTEL' 63) in Methanol-Water Solutions at 25 °C
 Obtained by Cooling Nearly Critical Solutions to 25 °C.

<u>Methanol in Methanol-Water Solvent, % by Weight</u>	<u>Nylon - Parts by Weight per 100 Parts by Weight of Meth- anol-Water Solvent</u>
100.0	4.68
93.9	5.11
86.6	6.46
82.1	5.64
76.5	4.57
74.0	2.20
61.9	0.212
50.4	0.111
39.4	0.109
28.9	0.076

Table 2

SOLUBILITY OF 'ZYTEL' 63 IN PARTS BY WEIGHT PER 100 PARTS
BY WEIGHT OF METHANOL-WATER SOLVENT



METHANOL in METHANOL-WATER SOLVENT, % by Weight

Figure 4

5. Stability of Solutions

Nylon solutions prepared by the first method became cloudy with time while those of the second method not only became cloudy, but acquired the consistency of a gel. While in the 'Water Wheel' Apparatus all solutions retained their fluid properties. Solutions prepared by the second method acquired the form of a gel in a short time if they were not subjected to continuous agitation.

The curve in Appendix I shows average gel time versus resin content of solutions for 'ZYTEL' 61 dissolved in ethanol-water solutions. It is shown because it parallels the observed results obtained from 'ZYTEL' 63 dissolved in methanol-water solutions.

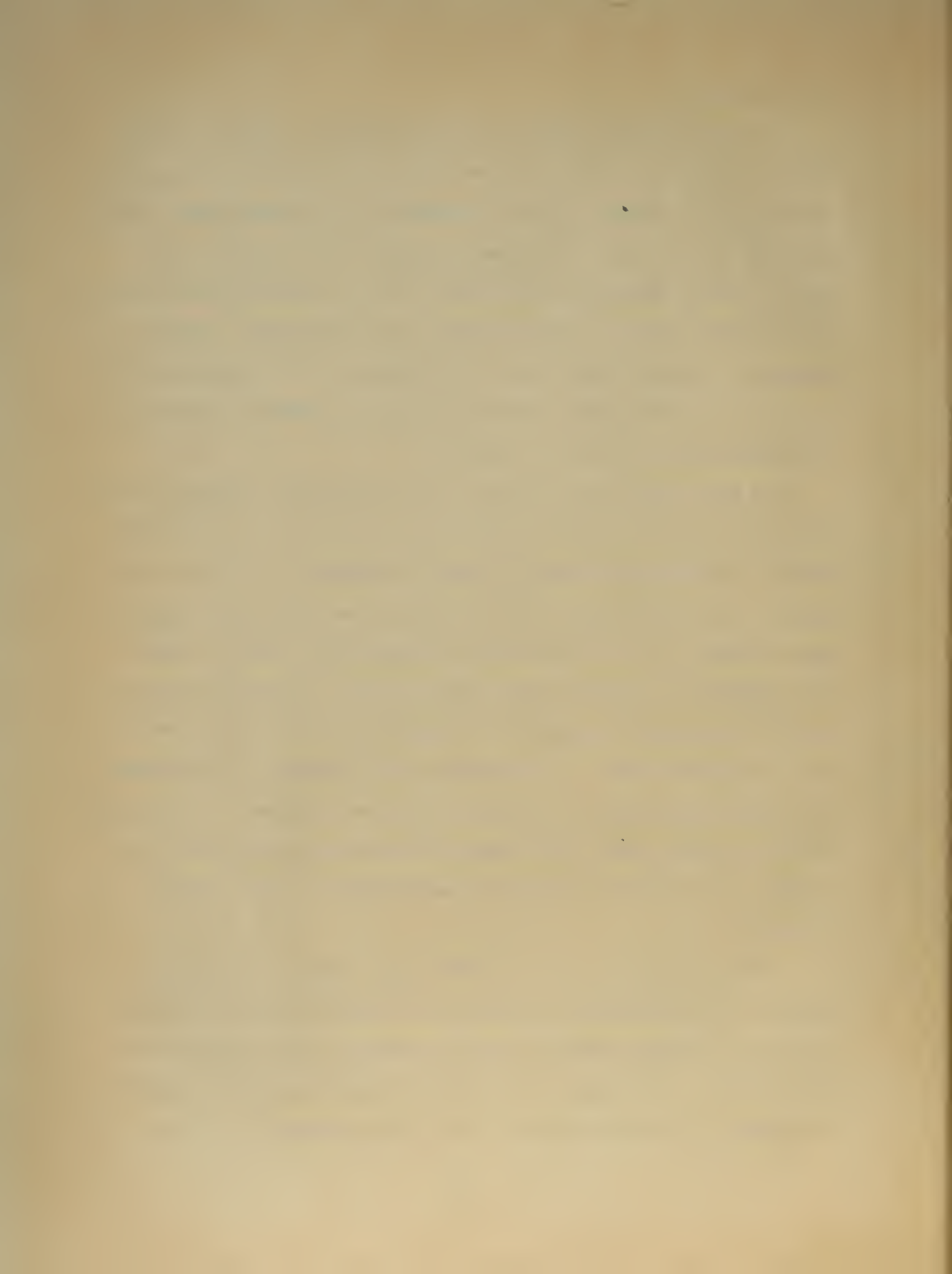
Cloudy or gel solutions of nylon became clear when heated. Even those solutions which gelled completely became fluid and clear when heated.

6. Conclusions

The amount of nylon dissolved in methanol-water solutions at 25 °C reached a maximum in several days and remained constant over a four month testing period. Hence, it can be assumed that the systems reached equilibrium and that the data as tabulated in Figure 1 are solubility data. This is further substantiated by the fact that the data obtained by approaching saturation from the unsaturated side were reproducible. Graphical interpretation of the data shows that the solubility of nylon in methanol-water solutions at 25 °C reached a maximum when the % by weight of methanol in the methanol-water solvent was about 82.

The data obtained by analyzing the nylon solutions, prepared by cooling nearly critical solutions to 25 °C, are considered to be only representative of the type of data that might be obtained. At elevated temperatures the resin content of nylon solutions can become quite high and upon cooling to 25 °C the nylon solutions become gels within 1-2 days. Consequently, the solutions were prepared so that, once they were cooled to 25 °C, they would not acquire the consistency or form of a gel within a relatively short time. By varying the time of exposure of the systems to elevated temperatures, a few sets of data were obtained. When plotted, the data yielded curves, all of which had the same general shape. For example, one curve plotted above and another below the curve shown in Figure 4.

The solubility data in the 60-100% range, obtained by analyzing nylon solutions prepared by cooling nearly critical solutions, appears to be very dependent upon the variables involved in the preparation of the solutions. For example, six solutions (Containing 84.7% by weight of methanol in the methanol-water solvent) were prepared as follows:



- a) Two methanol-water solutions containing 11 g of resin were heated at 65 °C for 60 minutes and cooled to 25 °C.
- b) Two methanol-water solutions containing 11 g of resin were heated at 65 °C for 40 minutes and cooled to 25 °C.
- c) Two methanol-water solutions containing 13 g of resin were heated at 65 °C for 60 minutes and cooled to 25 °C.

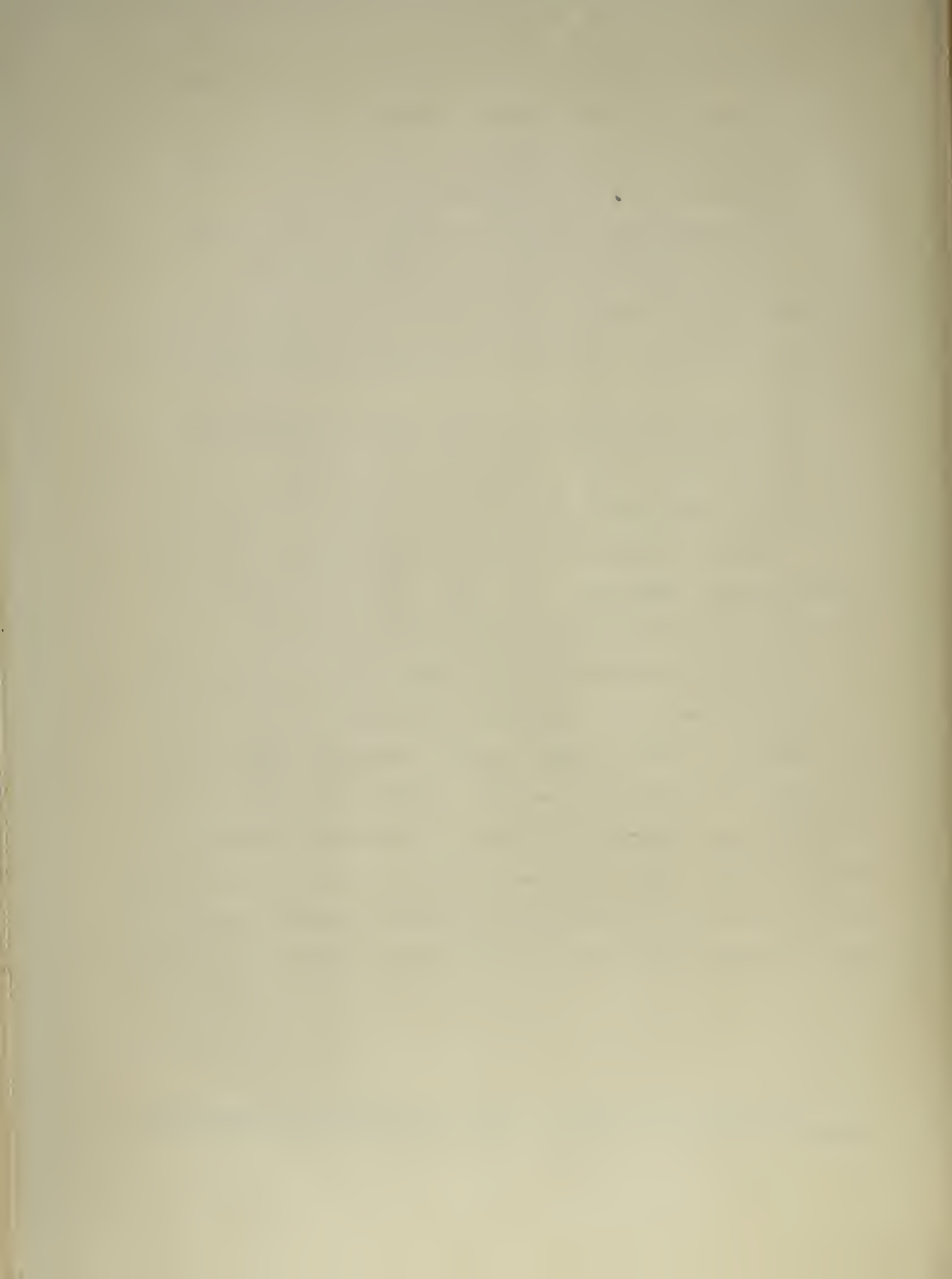
No positive means of agitation was provided for any of the systems during their preparation. The results of resin analysis were significant in that:

1. The resin content of the two solutions in a) differed from each other by 0.5%, in b) by 5% and in c) by 63%.
2. The average resin content of the solutions in b) was greater than the average resin content of the solutions in a) by 59%.

These deviations changed very little over a five week period and were much greater than the analytical error which was about 0.5%.

According to Hildebrand and Scott², fractional precipitation takes place whenever nearly critical polymer solutions are cooled. In such a fractionation the higher molecular weight fractions precipitate first followed by the lower weight fractions. However, the precipitation of some of the lower weight fractions takes place along with the higher weight fractions. Thus, the disparity of the resin content in two identically prepared nylon solutions may be attributed in part to the different average molecular weights of the resin existing in each of the solutions.

²Hildebrand, J. H., and R. L. Scott, The Solubility of Non-electrolytes 3rd Ed pp 376-377 Reinhold Publishing Corp. N. Y.



APPENDIX I

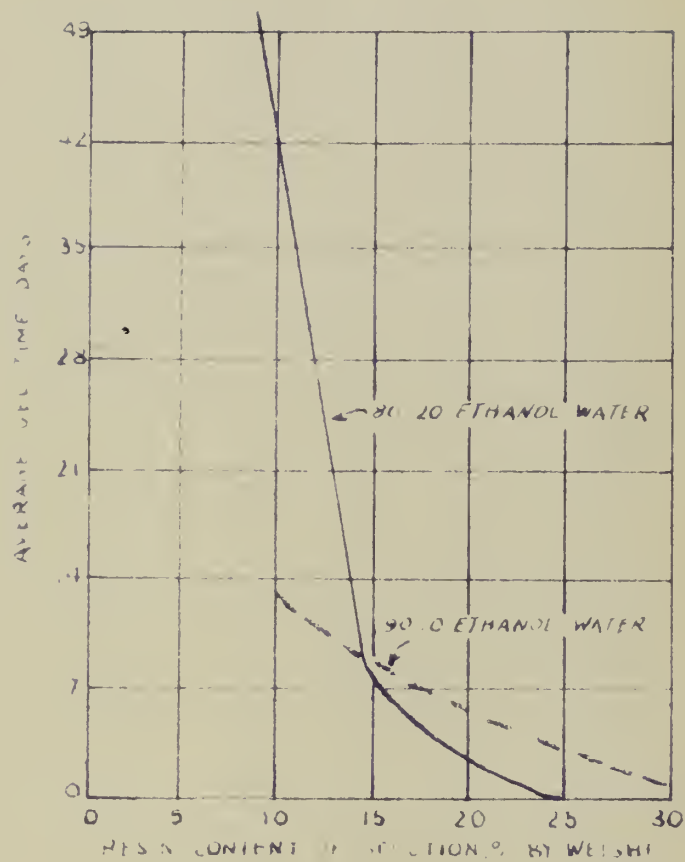
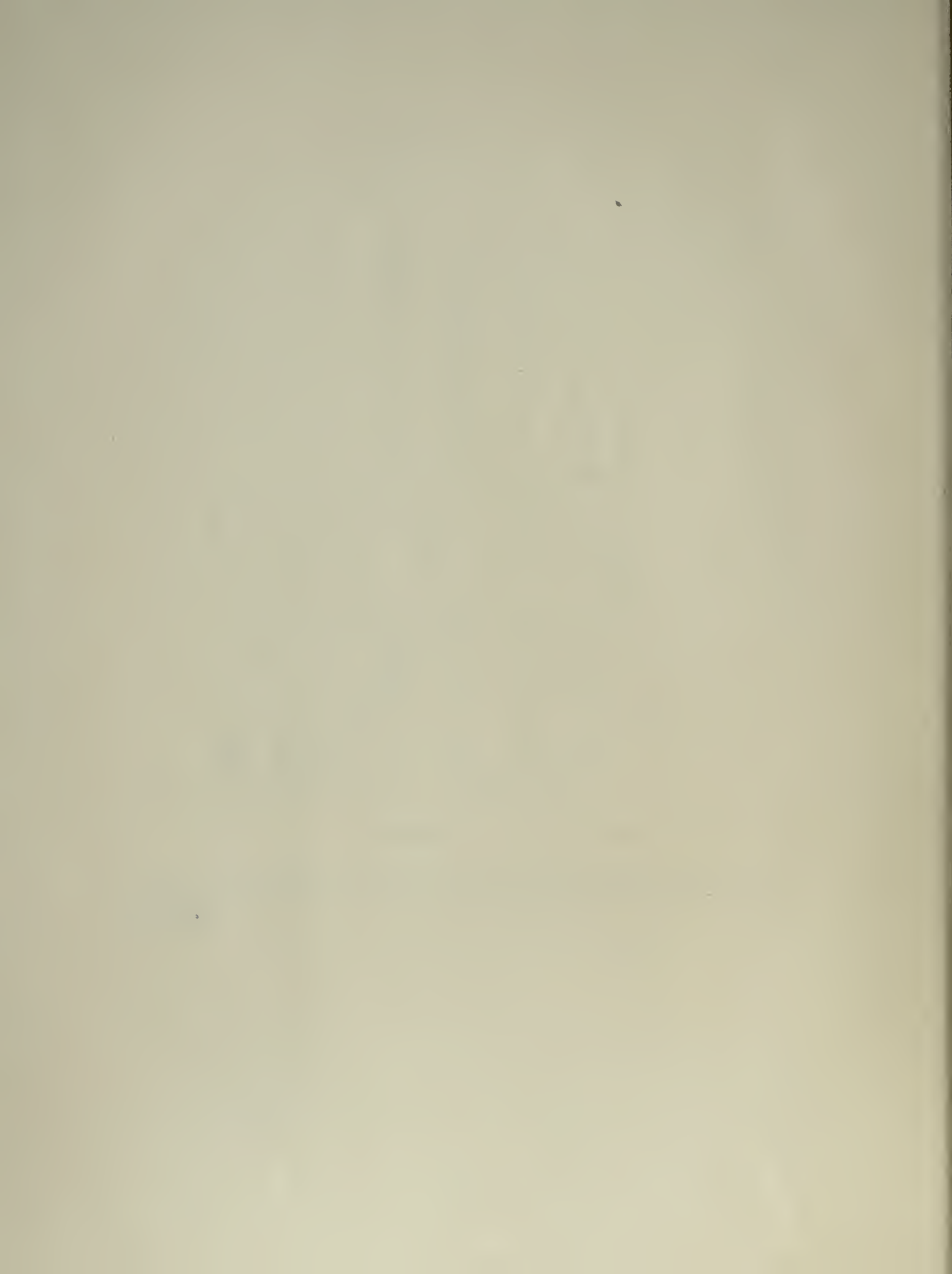
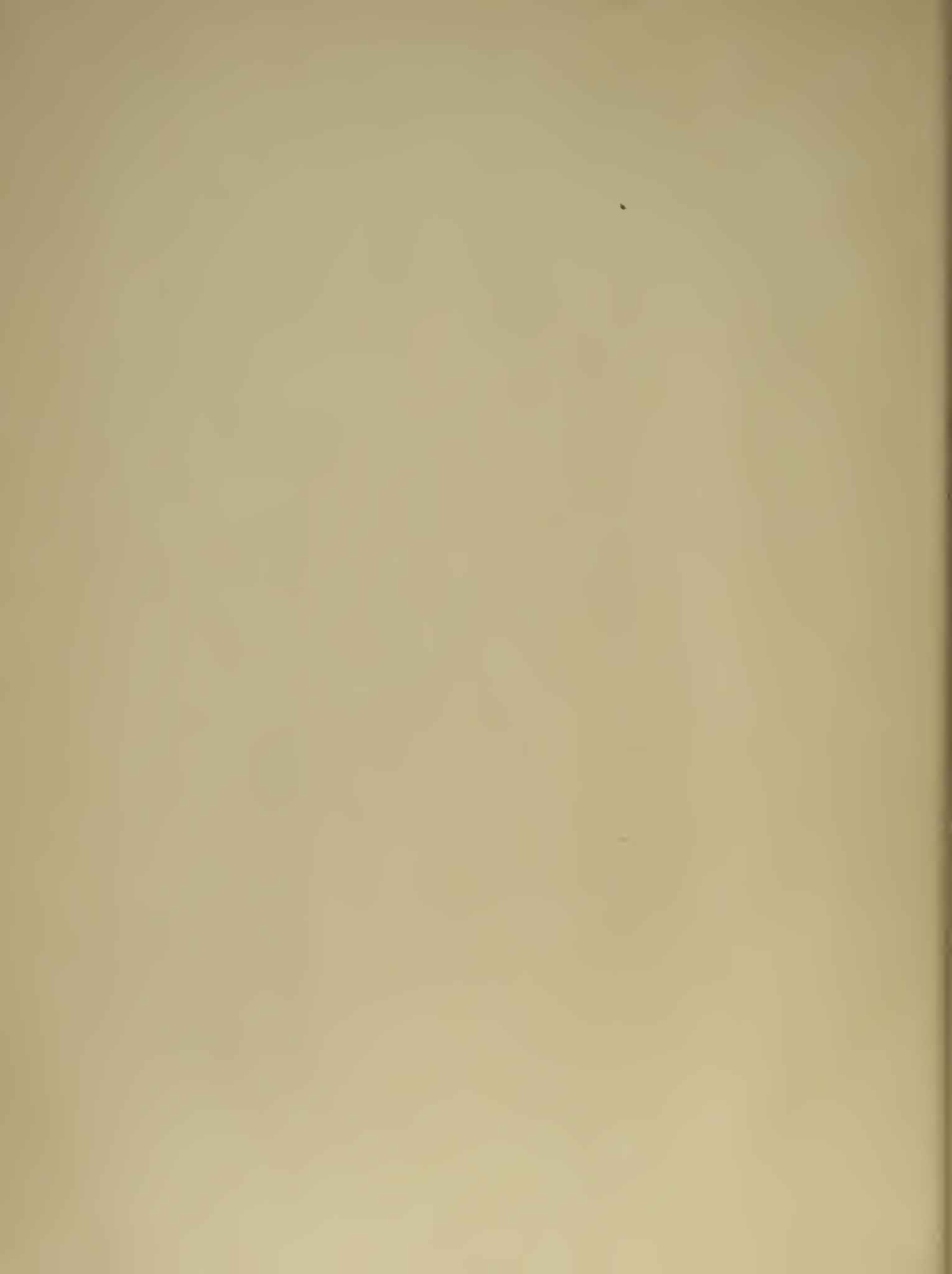


Figure 5

* The curve above was obtained from: DUPONT INFORMATION BULLETIN
No. X-56b





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Solubility of nylon in methanol-water so



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